

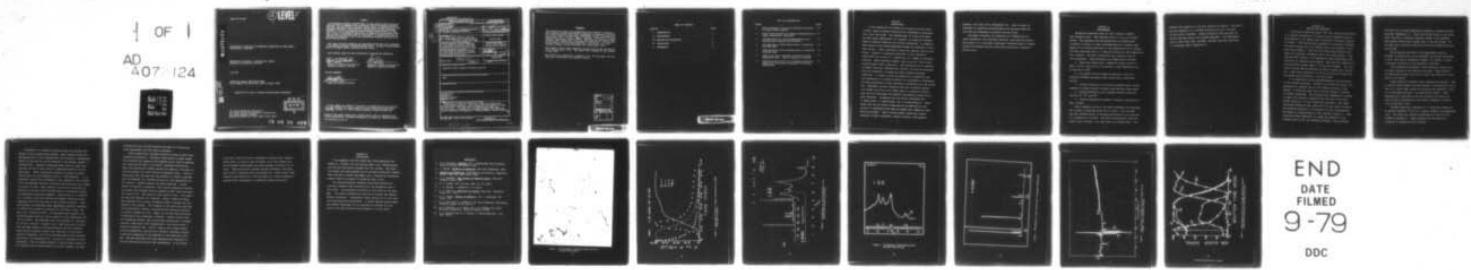
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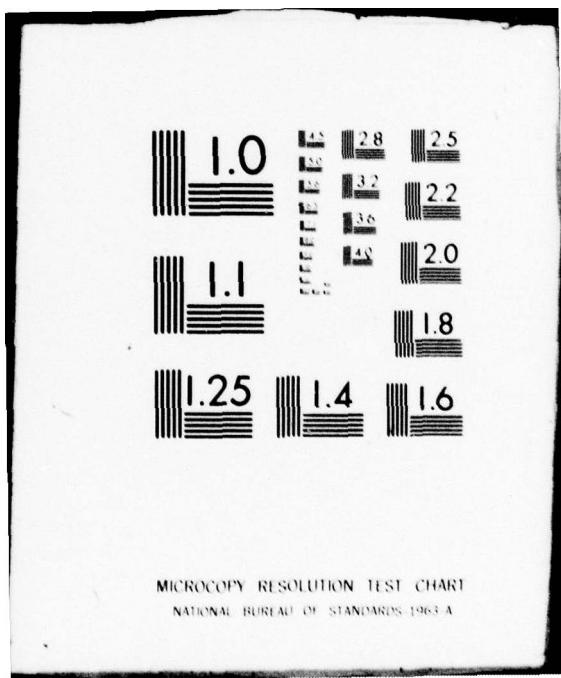
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EVALUATION OF THE USE OF CORROSION INHIBITORS AT THE ANODIC
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Mechanics and Surface Interactions Branch
Nonmetallic Materials Division

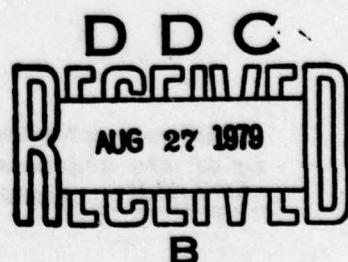
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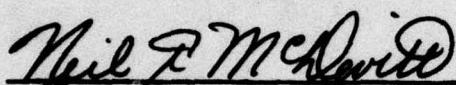
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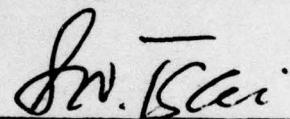
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Aluminum alloy, 2024, was treated with a number of solutions having corrosion inhibitor properties. These surfaces were then anodized in a H ₃ PO ₄ acid electrolyte. After anodization, the specimens were dipped into a 10% salt solution. A chromate solution-anodized composite film showed some corrosion improvement when compared to a standard phosphoric anodized specimen.		

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FOREWORD

This technical report was prepared by Neil McDevitt, Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Wright Patterson Air Force Base, Ohio, and Mr. James S. Solomon, University of Dayton Research Institute, Dayton, Ohio. The work was initiated under Project 2419 "Nonmetallic and Composite Materials", and was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

This report covers work conducted inhouse during the period May 1978 through April 1979. The report was released by the author in May 1979.

The authors are especially grateful to Mr. William Baun for his technical assistance and valuable advice.

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SECTION I INTRODUCTION

In the manufacture of present day military aircraft metal-to-metal adhesive bonded structures are considered an advantage over rivets and welds. The disadvantages of rivets and welds are well known (References 1-3); however, the apparent disadvantages of adhesive bonds are not totally documented. An adhesive bond relies on the forces generated between two surfaces in intimate contact. These interfacial forces are commonly known as adhesion. Adhesion is generally described in the literature (References 4-6) by one or a combination of a number of different theories. These theories; however, deal only with initial bond strength under static conditions. The performance of an adhesive-bonded structure, designed for aircraft, can only be evaluated from the standpoint of durability under stress-environment conditions. In order to have the capability of predicting the life expectancy of a bonded structure it is necessary to determine the aging resistance of each interface incorporated into the structure. Therefore, we must recognize that each interface created in a bonded joint has to be looked upon as a potential failure site until we understand the chemical and physical properties of each interface. Interfaces that are easily recognized are: 1) metal-oxide; 2) oxide-primer, and 3) primer-adhesive. Interfaces that are not easily recognized can be generated by the variety of ingredients that make up present day commercial adhesives and primers. Some of these organic resins may contain inorganic fillers, modifiers, organic solvents, antioxidants,

pigments, and scrim cloth (References 7,8). Some of these ingredients can generate microinterfaces with the bulk resin and must also be recognized as potential failure sites.

This report evaluates the possibility of removing one of these ingredients, the corrosion inhibitor, from the bulk primer and placing it at the anodic oxide-metal interface where it should perform its desired function while doing away with a potential failure site.

SECTION II EXPERIMENTAL

Rectangular specimens were cut from a sheet of 2024-T3 bare aluminum alloy. Each specimen was 5.0 x 2.5 x 0.05 centimeters. The specimens were pretreated with an acetone wipe, ultrasonic cleaning in carbon tetrachloride for 5 minutes, submerged in 0.1N sodium hydroxide at room temperature for 2 minutes, and then deoxidized with a 5:1 $\text{HNO}_3:\text{HF}$ solution at room temperature for 3 minutes. The metal surface was then treated to one of five procedures. These procedures are summarized as follows:

A. Films were formed from a commercial primer slurry of BR127, using a cure cycle of 45 minutes at room temperature and 30 minutes at 250°F.

B. Dry powder film was formed by spraying a slurry of strontium chromate and methyl ethyl ketone onto a warm metal surface.

C. Cathodic deposition of strontium chromate from a slurry composed of several organic solvents, Epon 508 and curing agent.

D. Surface generated by ion exchange reaction using the cations Ca^+ , Sr^+ , and Ba^+ .

E. Coatings generated by chromate conversion application to metal surface.

After treatment by one of the above procedures the specimens were rinsed in deionized water and air dried. Each specimen was then anodized using a 1.0M H_3PO_4 electrolyte with an applied D.C. potential of 10 volts. The time of anodization varied between 2 and 5 minutes. All tests were run as duplicates. One

specimen was exposed to a 10% salt solution by dipping. The specimen was subjected to a 30-second solution dip with a 4-minute air-dry cycle in between. Surface analytical data was then obtained from the control and corroded specimens. The instruments used in this study (AES, ISS/SIMS, and SEM) have been described in a previous report (Reference 9).

SECTION III RESULTS AND DISCUSSION

A corrosion inhibiting primer (CIP) can usually be described as a coating consisting of a slurry of solid inorganic particulate material in an organic resin containing substantial amounts of solvent. CIP's have proven successful in providing increased corrosion protection to the adhesive bond line; however, it has been found (Figure 1) that the solid particulate material will remain as individual islands on top of the oxide surface. This same specimen (Figure 1) was analyzed by Auger spectroscopy and strontium and chromium were detected. The corrosion inhibitor in this particular primer (BR127) is strontium chromate. This compound is being used successfully as part of present day technology. Under these conditions we can see how the solid particles can become microinterfaces in the bulk primer.

It is important to avoid misunderstanding the significance of the present discussion. Primers, as we know them today, are a necessity for industry and for the present are here to stay. However, it should be clear that we should attempt to improve on current technology. The following data represents an attempt to remove the corrosion inhibitor from the bulk of the resin primer and place it at the oxide-metal interface. The copper containing aluminum alloys (2024 and 7075) are known to accelerate aluminum corrosion in the presence of ionic contamination, and copper is always present at the interface (Figure 2). From a previous study (Reference 10) copper was detected in the corrosion pits of all the specimens analyzed. This localized

corrosion has also been observed on aluminum in aqueous chloride solutions (Reference 11). Since the pitting occurs at the oxide-metal interface a corrosion inhibitor placed on this surface would serve a more useful purpose than in the bulk primer. At the same time a potential failure site would be removed from the bulk primer.

The procedures described in the experimental section, followed by anodization, do not represent any current technology. In fact, they are an "Edisonian" attempt, in a sense, to place a corrosion inhibitor at the oxide-metal interface.

Films prepared by procedure A were completely removed from the metal surface by the anodization process. Auger analysis of these anodic oxide films did not detect any strontium or chromium on the surface.

Films formed by procedure B were anodized and analyzed. Most of the dry yellow powder film was removed in the anodization process, but a small Auger signal for strontium was observed at 1650 eV at high amplifier gain. No chromium was evident. These specimens were subjected to the salt solution and showed the same corrosion performance as the control (phosphoric anodize with no inhibitor film).

Cathodic deposition (procedure C) of strontium chromate at an applied potential of 15V for 2 minutes formed a non-homogeneous film. The cured film reacted to anodization as did the film formed by procedure A. Auger analysis did not detect any strontium or chromium at the interface.

Procedure D is a method of placing group IIA fluoride compounds on the aluminum alloy surface. When aluminum alloys are deoxidized with a nitric-hydrofluoric acid solution a considerable amount of fluoride ion can be detected on the surface (Figure 3, ISS spectrum). Rinsing in deionized water does not remove the fluoride ion and it most likely is chemically bound to the surface as AlF_3 . After rinsing this surface in running tap water calcium ions are also detected (Figure 3, SIMS spectrum). It is reasonably certain this represents a CaF_2 compound on the surface. Since the compounds calcium, strontium, and barium are only slightly soluble in water, these materials could act as corrosion retardants by reacting with available moisture and slowly forming the appropriate hydroxide compound. Since the pH in a corrosion pit is highly acidic the alkaline environment created by these compounds would slow the rate of the corrosion reaction. After pretreatment (as described under experimental section) specimens of 2024-T3 were placed in solutions of 0.2M CaCl_2 , SrCl_2 , and BaCl_2 for 5 minutes at 50°C. All specimens were rinsed in agitated deionized water for thirty minutes at room temperature and then air dried. The specimens were then anodized in 1.0M H_3PO_4 at 10V for 2 minutes. Figures 4 and 5 show data from a surface that had been soaked in strontium chloride and then anodized. These spectra represent typical data obtained for the overall series of compounds. All of the ISS/SIMS spectra were obtained using ^4He as the bombarding ion. Strontium is detected by both techniques. The ion exchange method of placing these cations on the aluminum alloy surface seems to be valid; however, the data

obtained from the 10% salt-solution dip does not indicate any large improvement over the control specimens.

Films formed from a chromate conversion solution were investigated by procedure E. The major constituents of these commercial solutions are generally ferricyanide salts, acidic chromates, and fluorides with most of the minor ingredients proprietary.

These non-electrolytic formed coatings are used as a corrosion inhibiting surface on a wide variety of aluminum alloys. Figure 6 shows Auger data obtained from the surface of a 2024-T3 specimen that was immersed in a chromate solution at room temperature for six minutes. Chromium signals are easily detected. A small amount of fluoride is observed. This coating completely obscures any signal from aluminum that was scanned at four times the amplifier sensitivity. The coating is dark gold in color. This specimen was then anodized for 5 minutes. Figure 7 shows the Auger data obtained from an argon ion-sputter profile through the film formed on this surface. The intensity of the gold color was less after anodization; however, the profile data indicates chromium is present through the film. Copper, as we have seen previously, is detected at the oxide-metal interface. Sputter profile data of an anodized surface, that has not been treated with a chromate solution, shows very little phosphorous in the coating after 2 minutes of sputter time. Figure 7 shows a much longer sputter time for phosphorous indicating the chromate conversion coating allows more phosphorous to be adsorbed in the anodization process. The data obtained from these specimens when subjected to the 10% salt-solution dip are very encouraging. On two series

of corrosion tests the control specimens (anodized only) showed a large amount of pitting after 60 hours, while the chromate-anodized prepared films showed only minor amounts of pitting at 100 hours. These preliminary studies indicate procedure E may have some value in improving bond line durability. Anodic oxide films formed by this method will form the basis of a future program to evaluate their performance in adhesively bonded structures.

SECTION IV CONCLUSIONS

It is apparent from this study that films physically adsorbed on a surface will not hold up under a D.C. applied potential and are very easily stripped from the surface. The group IIA cations show some possibility as corrosion inhibitors; however, there was such a slight improvement that a statistical evaluation program would be necessary to establish their value.

The chromate-anodized composite films show promise as a corrosion retardant when evaluated with the parameters used in this study. The parameters evaluated in this study do not represent the surface preparations required of present day adhesive bonding technology. Consequently these results are at this time only qualitative and approximate. A future program using present day surface technology will be required to evaluate the true value of the data obtained from procedure E of this study.

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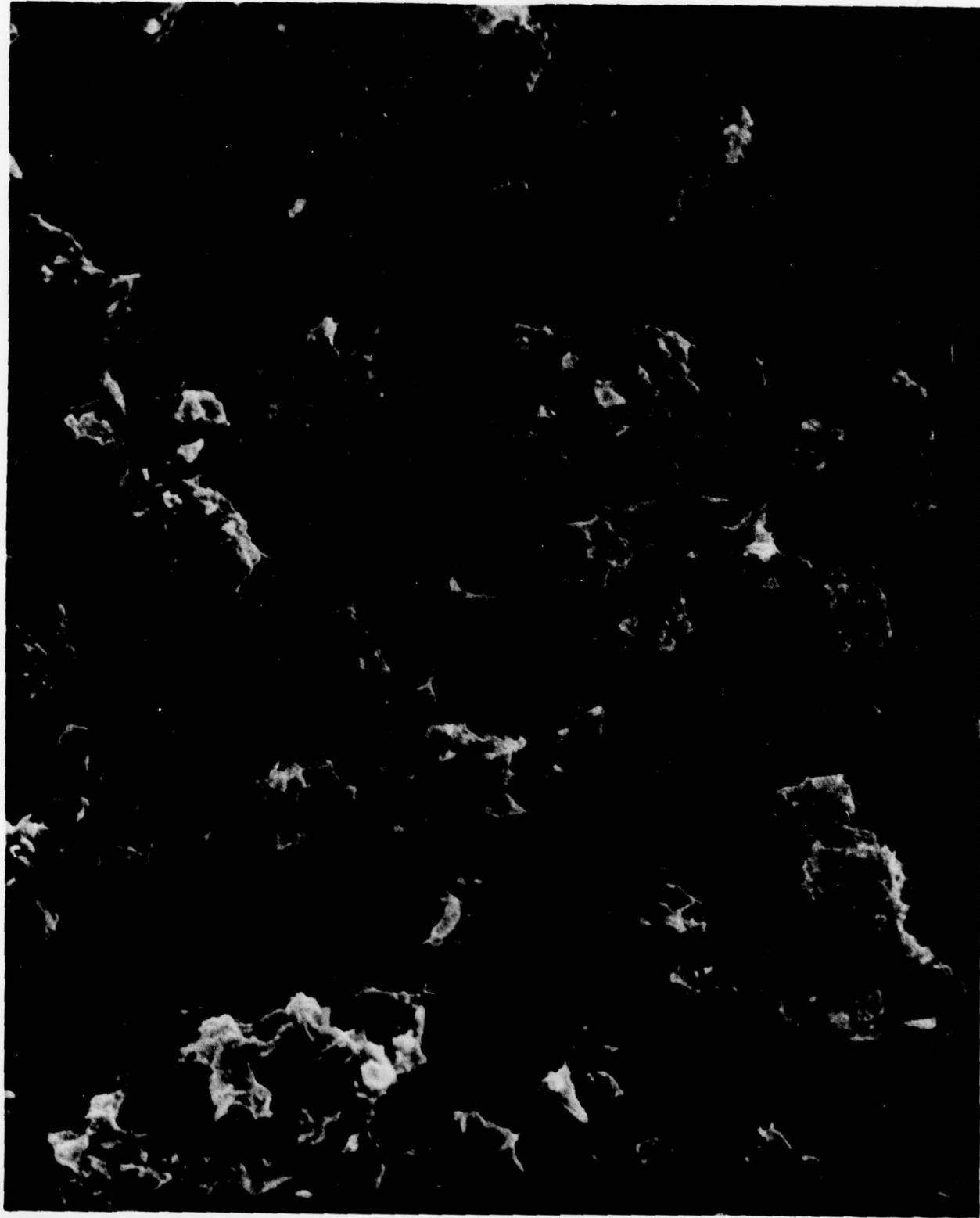


Figure 1. SEM Micrograph of Strontium Chromate Particles
on Anodic Oxide Coating.

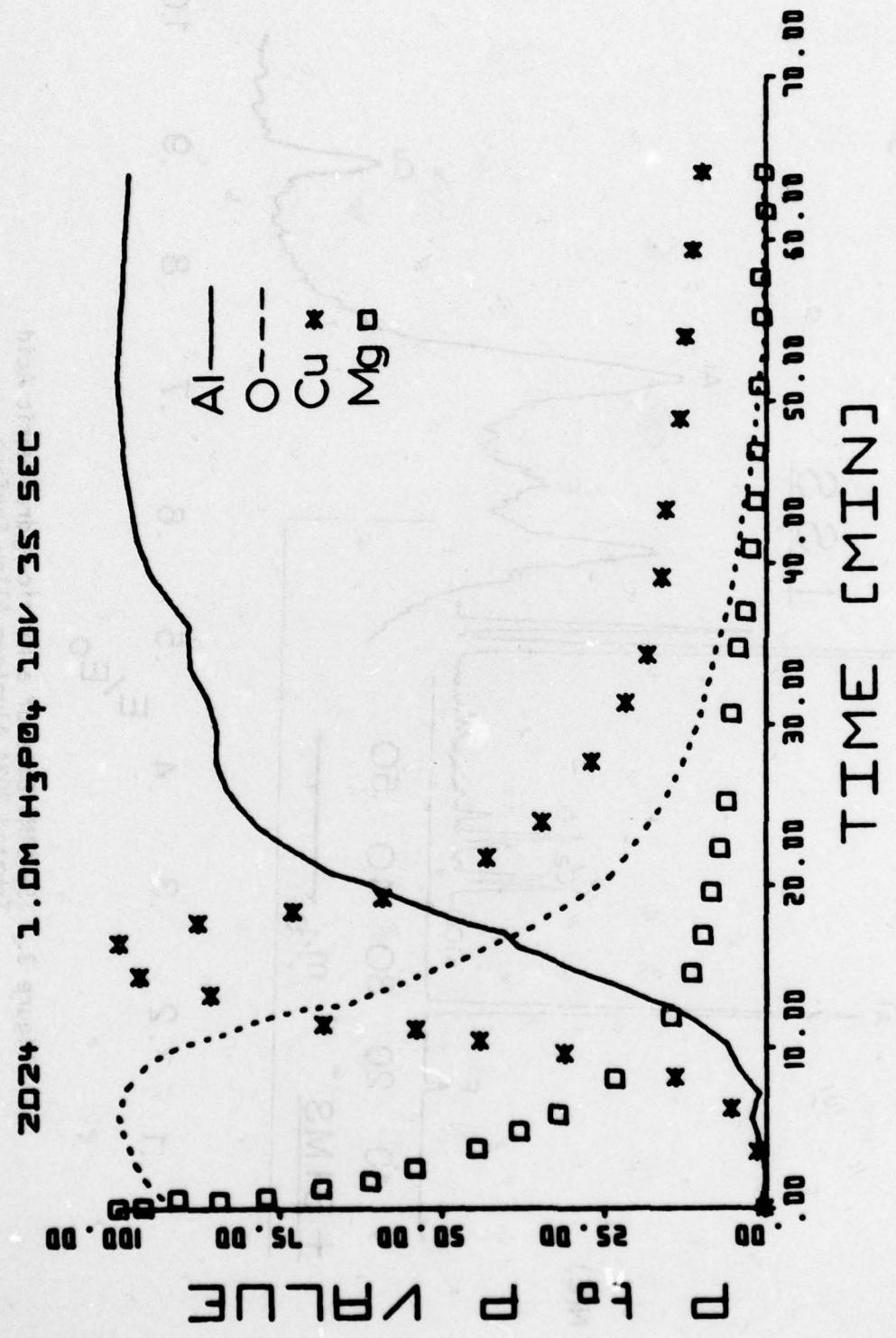


Figure 2. Auger Sputter Profile of Copper Concentration at Anodic Oxide-Metal Interface.

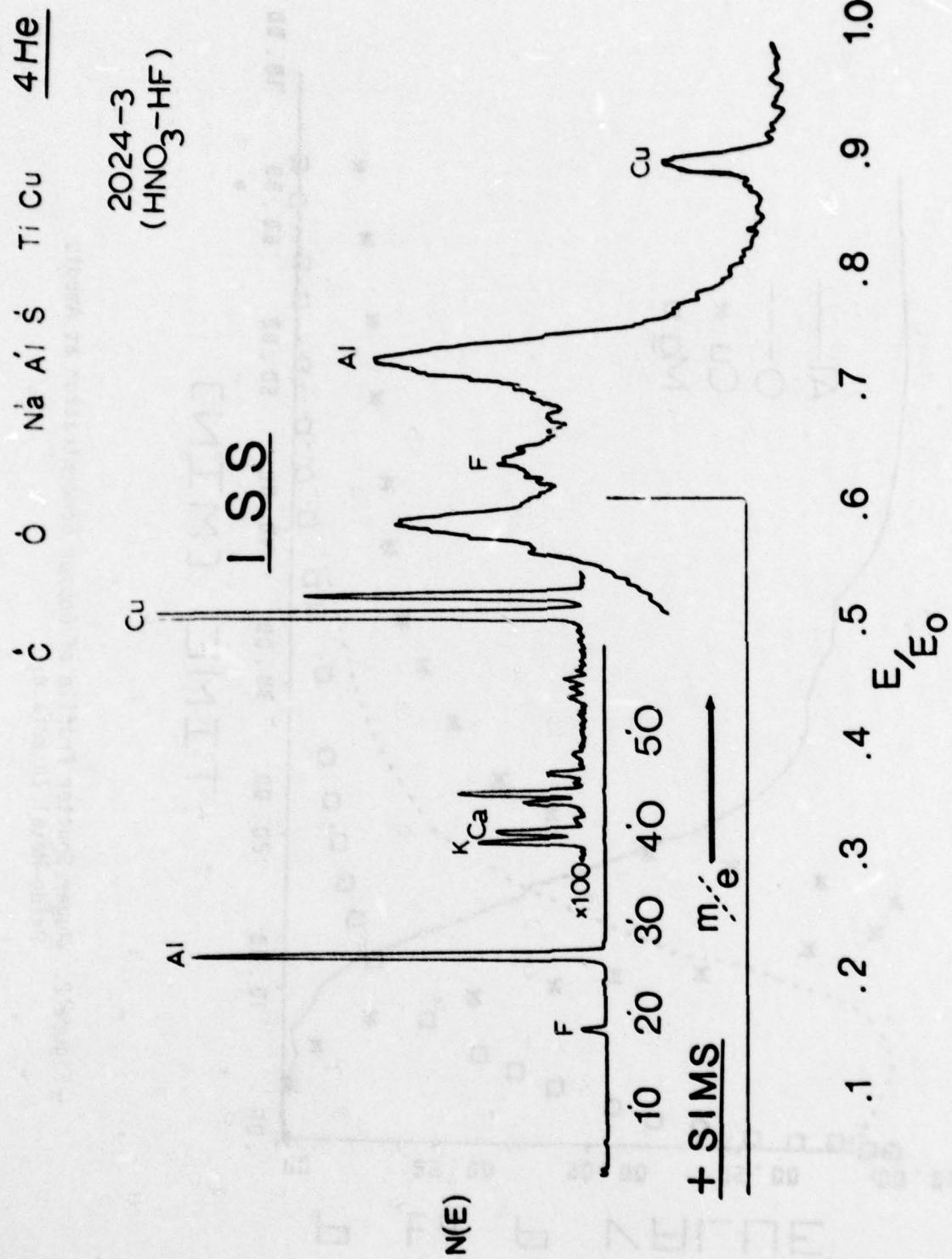


Figure 3. ISS-SIMS Data of a Nitric-Hydrofluoric Acid Treated 2024 Aluminum Alloy Surface.

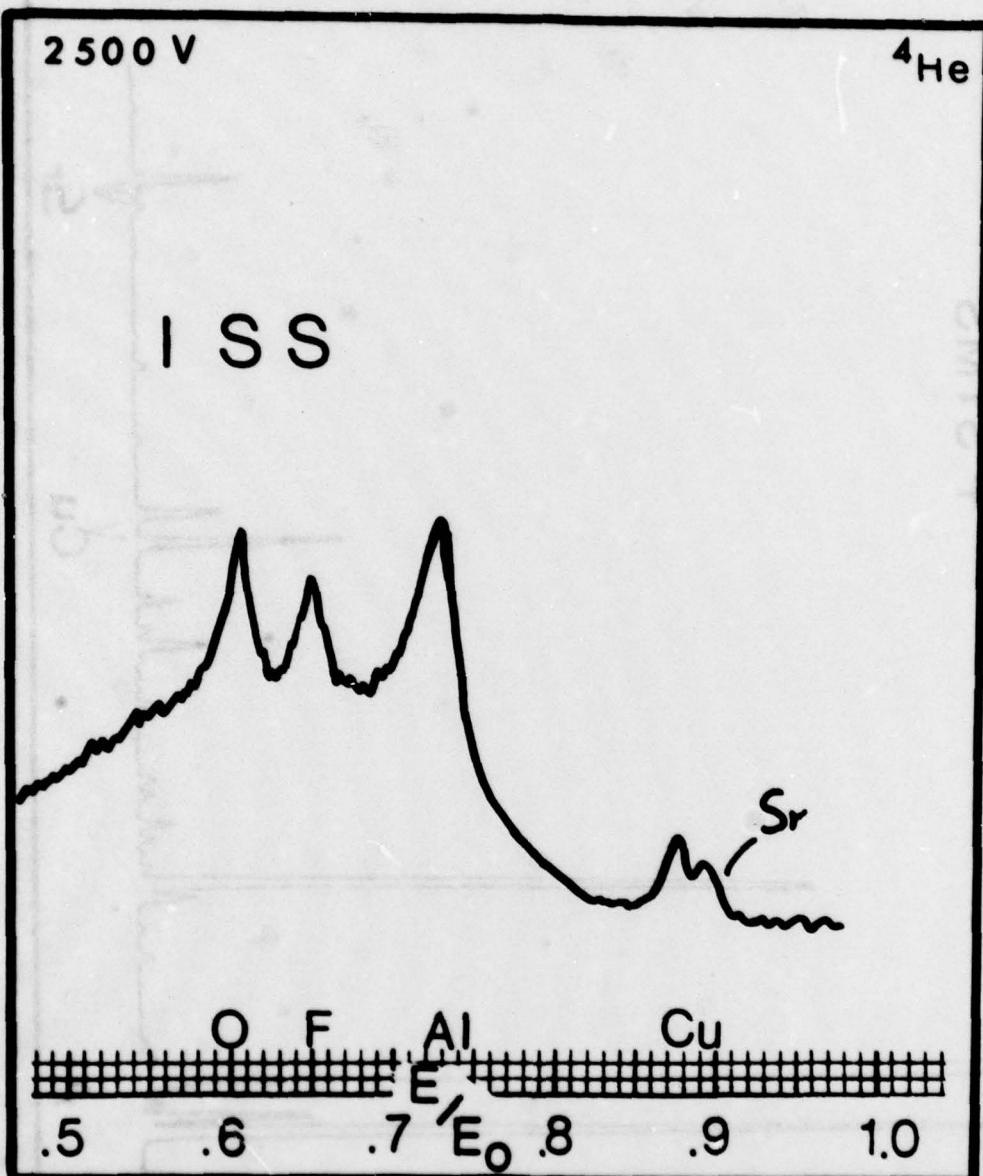


Figure 4. ISS Spectrum of 2024 Surface After a Strontium Chloride Soak.

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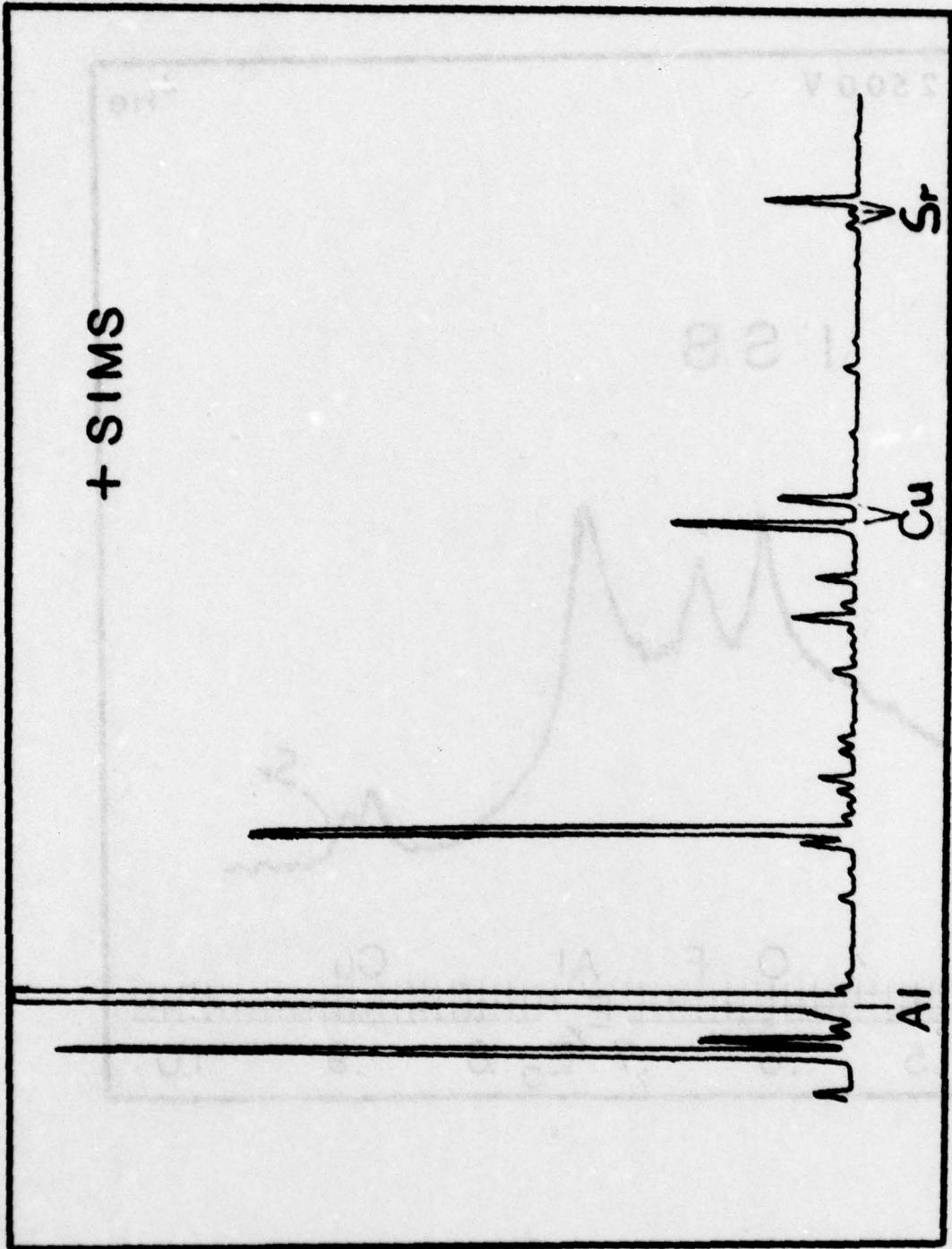


Figure 5. SIMS Spectrum of 2024 Surface After a Strontium Chloride Soak.

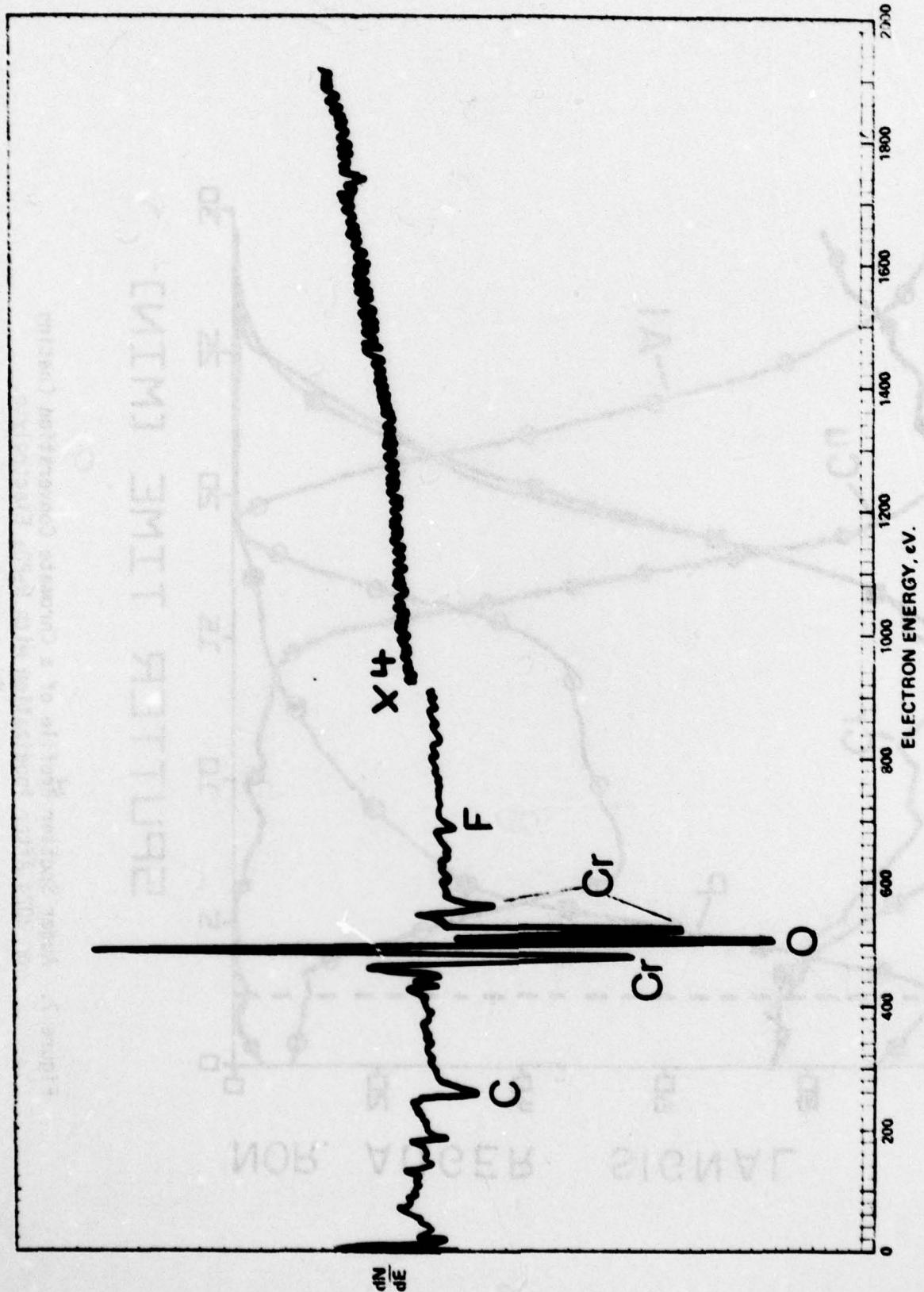


Figure 6. Auger Data from a Chromate Conversion Coated Surface of 2024. Time in Solution 6 Minutes.

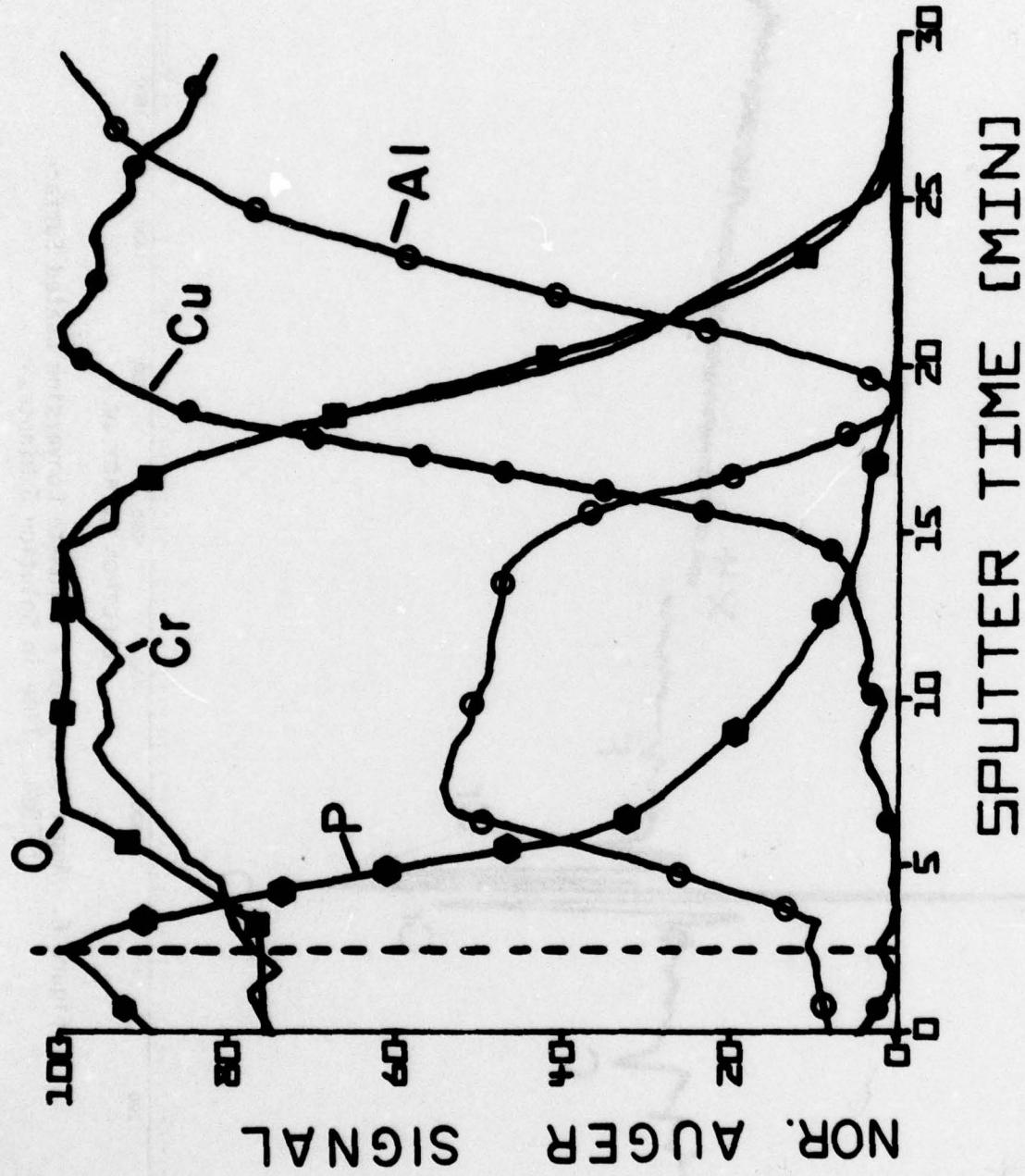


Figure 7. Auger Sputter Profile of a Chromate Conversion Coating on 2024 After Anodization with H_3PO_4 Electrolyte.